DETERMINATION OF INDIUM ON AN AC POLAROGRAPH

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Indium is usually determined polarographically in a hydrochloric acid supporting electrolyte. Under these conditions indium must be completely separated from cadmium, since the half-wave potentials of both elements are close to each other. When the test materials contain large concentrations of other elements, the greater part of them have to be removed beforehand, even when there is a large difference between their half-wave potentials and that of indium.

The use of an ac polarograph having a high resolving power permits indium to be determined without preliminary removal of the large excess of many accompanying elements. Nevertheless, even in this case, elements whose half-wave potentials are close to that of indium, in particular cadmium, interfere with determination of indium as a supporting electrolyte of hydrochloric acid.

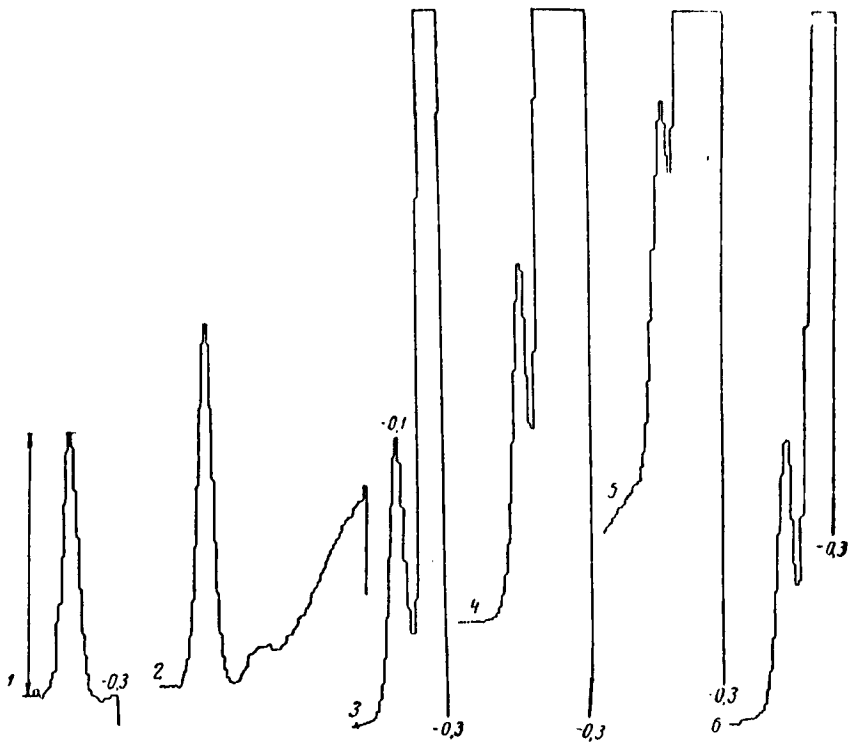

Fig. 1. Polarograms for 1 mg In/ml in the presence and in the absence of tin: Curve 1) Supporting electrolyte 13% HBr + 10% H_3PO_4; 2) 23% HBr; 3) 100 mg Sn/ml, 13% HBr + 10% H_3PO_4; 4) 100 mg Sn/ml, 23% HBr; 5) 300 mg Sn/ml, 23% HBr; 6) 300 mg Sn/ml, 13% HBr + 10% H_3PO_4.

We have carried out some work in order to develop a rapid method for the determination of indium on an ac polarograph. The work was carried out on a "Mervyn" polarograph–Model 3 [1, 2, 3]; the anode was a mercury pool while the cathode was a dropping mercury electrode with a dropping time of 2.8-3.5 sec. Methods have been published on the use of this polarograph for the determination of copper, lead, cadmium, nickel, zinc, indium, chromium, and uranium in steels, pure metals, and alloys based on aluminum, magnesium, zinc, tin, and copper [4-7].

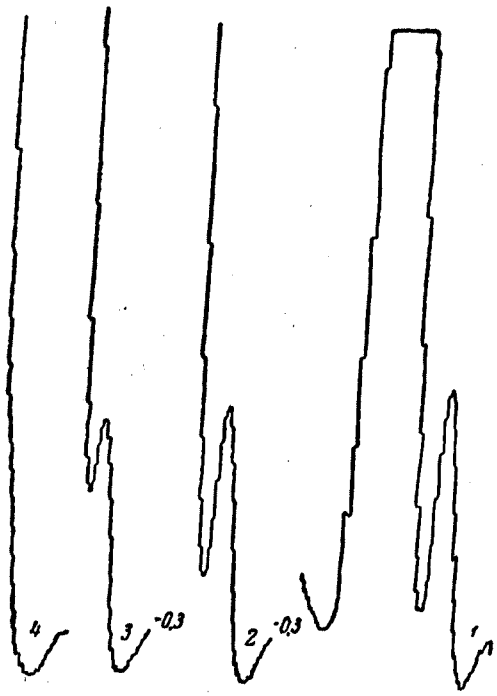

Fig. 2. Polarograms for 1 mg indium/ml in the presence of 20 mg cadmium 1 ml at various hydrobromic and phosphoric acid concentrations. Curves 1-4, supporting electrolyte 23% HBr; 18% HBr + 5% H_3PO_4; 13% HBr + 10% H_3PO_4; 8% HBr + 15% H_3PO_4.

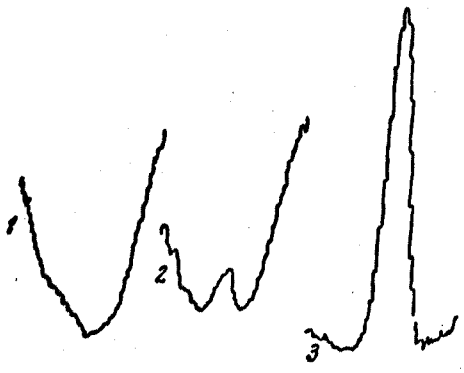

Fig. 3. Polarograms of indium in a supporting electrolyte which contains 13% hydrobromic acid and 10% phosphoric acid; 1) Supporting electrolyte in the absence of indium - 2) 0.01 mg In/liter; 3) 0.08 mg In/ml.

In order to obtain separate the indium and cadmium waves, Cozzi, Vivarelly, and Bulavova [8, 9] suggested a supporting electrolyte containing Br^- and Cl^-. Under these conditions the half-wave potentials of indium and cadmium differ from each other by 0.2 v, this is explained by the difference in the stability of the chloride and bromide complexes of indium ($pKInBr_3 = 2.48$, $pK\ InCl_3 = 3.23$), and by the formation in bromide and chloride solutions of stable cadmium complexes whose instability constants do not differ much from each other ($pH\ CdCl_2 = 2.06$; $pK\ CdBr_2 = 2.34$) [10].

According to published results [8, 9] reduction of indium in the supporting electrolytes is reversible and is a three electron process.

In the work described here, in order to determine indium in the presence of cadmium, the supporting electrolyte used was a solution of hydrobromic acid containing phosphoric acid. This electrolyte permits indium to be determined, not only in the presence of cadmium, but also in the presence of tin, since the latter forms a stable complex with phosphoric acid. It is known that in a supporting electrolyte of phosphoric acid, in the absence of halides, tin does not show up polarographically [7], in the presence of hydrobromic acid and phosphoric acid a peak for tin appears. Nevertheless, its peak height (Fig. 1) is considerably less than the peak height obtained when phosphoric acid is absent, and accordingly it interferes with the determination of indium to a lesser extent. At the same time, an increase in phosphoric acid concentration lowers the sensitivity with respect to indium, and lowers the resolution of indium and cadmium (Fig. 2). Accordingly, it was necessary to establish the optimum concentrations of hydrobromic and phosphoric acids, at which the sensitivity and the resolution would be acceptable, while interference from tin would be suppressed to a suitable extent. It was found that the optimum supporting electrolyte for the polarographic determination of indium in the presence of tin and cadmium, is a solution which is 13% with respect to hydrobromic acid and 10% with respect to phosphoric acid. Under these conditions there is a linear relation between indium concentration and the height of its maximum on the polarograms within the limits 0.01 mg/liter (10^{-7}M) and 80 mg/liter (10^{-3}M) at a ratio of Cd: In = 20 : 1 (Fig. 3).

For concentrating indium during the analysis of industrial products, it is usually precipitated with ferric hydroxide by means of ammonia. Indium is removed from the main bulk of all the elements which form soluble ammoniacal complexes, i.e., from copper, zinc, and cadmium whose contents are significantly higher than the indium content. It was also important to establish the half-wave potentials, and the reversibility of the reduction processes of the metals which separate out with indium during coprecipitation with ferric hydroxide in the course of an analysis. This is true in the main of lead, antimony, tin, selenium, and tellurium.

TABLE 1

The Half-wave Potentials and the Reversibility of the Reduction Processes of Certain Metals

Element	Supporting electrolyte	Concentration, ml	$E_{1/2}$, v	Half-wave potential σ, mv
In	13% HBr + 10% H_3PO_4	10^{-4}	—0.42	28,6
Cd	13% HBr + 10% H_3PO_4	10^{-4}	—0.50	46
Pb	13% HBr + 10% H_3PO_4	10^{-4}	—0.32	46
Fe	13% HBr + 10% H_3PO_4	10^{-4}	—0.33	57
Fe	8% HCl + 15% H_3PO_4	10^{-4}	—0.16	31
Te	13% HBr + 10% H_3PO_4	10^{-4}	—0.13	46
Te	13% HBr + 10% H_3PO_4	$2 \cdot 10^{-4}$	—0.33	Indistinct
Te	13% HBr + 10% H_3PO_4	$3 \cdot 10^{-4}$	—0.16	80
Te	13% HBr + 10% H_3PO_4	$4 \cdot 10^{-4}$	-0.62	46
Te	8% HCl + 15% H_3PO_4	10^{-4}	—0.16	34
Se	13% HBr + 10% H_3PO_4	10^{-4}	—0.32	23
Sb	13% HBr + 10% H_3PO_4	10^{-4}	—0.32	57
Sn	13% HBr + 10% H_3PO_4	10^{-4}	—0.14	Indistinct
Sn	13% HBr + 10% H_3PO_4	$2 \cdot 10^{-4}$	—0.31	46

The use of an ac polarograph makes it possible to assess [2, 11] the reversibility of processes on the basis of the half-wave width. For reversible processes:

$$\sigma = \frac{88}{n},$$

where σ is the half-wave width, mv; and n is the number of electrons participating in the reaction.

In Table 1 are given results for the half-wave potentials and width which we obtained for certain metals.

According to these results, tellurium ($E_{1/2}$ = -0.46; σ = 80 mv) should interfere with indium determination in a supporting electrolyte containing hydrobromic acid. Tin, selenium, antimony, iron, lead, and cadmium should interfere to a lesser extent. This was confirmed during a study of the effect of these elements on the polarographic determination of indium. It was established that the height of the indium maximum remains constant up to ratios of: Fe : In = 30000 : 1; Pb : In = 1000 : 1; Sb : In = 800 : 1; Sn : In = 250 : 1; Se : In = 80 : 1; Cd : In = 20 : 1; Te : In = 1 : 1.

Indium can be determined without using extraction, this significantly simplifies the analytical procedure and cuts down on the time.

When the iron content exceeds the indium content by more than 30,000 times, it is expedient to carry out the determination of indium in a supporting electrolyte containing hydrochloric and phosphoric acids (15% H_3PO_4 + + 8% HCl). Hydrobromic acid cannot be used, since in the presence of Br^- it is not possible to reduce trivalent iron to the divalent state, as this is usually done in a hydrochloric acid medium, because the covalent bonds between iron and bromine are more stable than those between iron and chlorine. Interference on the part of Fe^{3+} in a supporting electrolyte of phosphoric and hydrochloric acids is eliminated by using powdered iron as reducing agent. Phosphoric acid must be present in solution in order to suppress interference from tin, the peak height of which is thereby considerably decreased.

Judging from the half-wave width (σ), the reversibility of the reduction of tin in a supporting electrolyte of hydrochloric acid in the presence of phosphoric acid does not decrease, accordingly, the drop in the peak height can, apparently, be explained by a decrease in the diffusion coefficient.

TABLE 2

Results of the Polarographic Determination of Indium

Test material	Sample wt, and dilution, g/ml	Indium found, %		
		13% HBr + 10% H_3PO_4	8% HCl + 15% H_3PO_4	By a fluorescence method
Waelz oxide	0.2/25	0.005 0.005	0.005	—
Tin slag	1/10	0.0002 0.0001	— —	0.0002 0.0001
Waelz oxide	0.2/25	0.005 0.005	0.005	0.005
Neutral lead cake 111 Neutral lead cake 113	0.2/25 0.1/50	0.012 0.013	— 0.012	— 0.011
Acid lead cake 140	0.2/25	0.002 0.002	— 0.0025	— —
Acid lead cake	0.2/25	0.003 0.003	0.003 —	0.003 —
Electric filter 1 dust	0.5/25	0.0006 0.0007	0.0007 —	0.0007 0.0006
Electric filter 47 dust	0.5/25	0.0009 0.0008	0.0009 0.0007	0.0009 0.0007
Dust from reverberatory furnace 48	0.5/25	0.002 0.002 0.002	0.002 — —	0.002 0.002 —
Lead concentrate	1/25	0.0002 0.0002 0.0002 0.0001	— — — —	— — 0.0001 0.0002
Tin concentrate	0.2/25	0.0009	0.0008	0.001
Tin dust	0.2/25	0.005 0.005 0.005	0.0045 0.005 —	— 0.005 —

Cadmium must be completely removed from indium by two reprecipitations of the hydroxide precipitates.

In a supporting electrolyte of phosphoric and hydrochloric acids tellurium interferes to a lesser extent than in a supporting electrolyte of phosphoric and hydrobromic acids. This is explained by the large difference in the half-wave potentials of indium and tellurium in the first case (see Table 1), and also by the fact that reduction of tellurium in the presence of Cl^- proceeds more reversibly (σ = 34 mv) than in the presence of Br^- (σ = 80 mv).

Thus the greater the half-wave width of the accompanying element, the greater the extent to which it interferes with the determination of the test element.

Results of analyses* of industrial products are given in Table 2.

* N. P. Khairulina analyzed the samples.

Analytical Procedure (For samples with Fe : In <30,000 : 1)

A 0.1-1g sample, depending on the expected indium content, is decomposed in a mixture of hydrochloric and nitric acids. When large amounts of silica are present, decomposition is carried out in the presence of ammonium fluoride. Lead sulfate is then separated after evaporating the solution with sulfuric acid to the appearance of sulfur trioxide fumes. The lead sulfate precipitate is filtered off on a fine filter and washed with a 1% sulfuric acid solution. To the filtrate is added 25% ammonia solution in order to precipitate the hydroxides of iron and indium. The precipitate is washed 1-2 times with a hot 5% solution of ammonium chloride containing a small amount of ammonia; reprecipitation is carried out and the precipitate again washed. The precipitate is dissolved in the minimum amount of hot hydrochloric acid (1 : 1), the solution being collected in the same flask as that from which the filtration was carried out. The liquid is evaporated almost to dryness, the residue is moistened with concentrated hydrobromic acid containing 2-3 drops of bromine, and it is again evaporated almost to dryness. To this residue is added 13 ml of hydrobromic acid (1 : 3) and the solution transferred to a 25 ml standard flask, 10 ml of phosphoric acid (1 : 3) is added, and the volume made up to the mark with water. After mixing, part of the solution is transferred into a vessel through which nitrogen can be passed; nitrogen is passed through the solution for 5-10 min, and polarograms are taken in an apparatus to which an ac voltage is applied in an electrolyzer with a mercury pool electrode.

The half-wave potential of indium is -0.42 v. Calculations are made on the basis of standard curves.

Analytical Procedure (For samples with Fe : In 30,000:1)

A 0.1-1.0 g sample is decomposed as described above. After removing lead sulfate and precipitating ferric and indium hydroxides, the latter are reprecipitated twice. The precipitate is washed with hot 5% ammonium chloride containing some ammonia, and it is then dissolved in 8 ml hydrochloric acid (1 : 3). The solution is transferred to a 25 ml standard flask, 15 ml of phosphoric acid (1 : 3) is added and the volume made up to the mark with water, and the whole mixed. To an aliquot of the solution is added, on a spatula tip, iron powder reduced with hydrogen. After the liquid has been decolorized and turbulent evolution of hydrogen has ceased, the residual iron is filtered off, and the solution is transferred to an electrolyzer to take polarograms. The half-wave potential of indium is -0.6 v.

Analytical Procedure (For slags and tin samples)

A 0.1 g aliquot, for contents of thousandths and hundredths of a percent of indium, and 0.5-1.0 g for even smaller contents, is mixed in a nickel crucible with 7-8 g of sodium peroxide, the mixture is covered with 1-2 g of sodium peroxide and is fused in a crucible oven at 600-650° for a few minutes until a homogeneous liquid melt is obtained. The hot crucible plus the melt is carefully lowered into a beaker of cold water in order to remove the outer clinker, care being taken to avoid water getting into the crucible. In order to leach the melt, the cooled crucible is placed in a 300-400 ml beaker, into which 50-60 ml of water has been poured beforehand, and the beaker is covered with a watch glass. After leaching, the crucible is removed from the beaker and washed with hot water.

The volume of the solution in the beaker is adjusted to 200-250 ml with water. The liquid is filtered through a coarse filter. The residue is washed twice with hot 2% alkali solution and dissolved in the wrapped up filter paper with hot hydrochloric acid (1 : 1), after which the ferric and indium hydroxides are reprecipitated with ammonia. The procedure outlined above is then followed.

SUMMARY

A method has been developed for the determination of indium contents down to 10^{-7}M. The analysis is carried out on an ac polarograph with high resolving capacity; this permits determinations to be carried out at ratios of Fe : In = 30,000 : 1; Pb : In = 1,000 : 1; Sb : In = 800 : 1 etc. The supporting electrolyte is a solution which is 13% with respect to HBr and 10% with respect to H_3PO_4. Determinations can be carried out in the presence of cadmium.

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POLAROGRAPHIC DETERMINATION OF MICROGRAM AMOUNTS OF ARSENIC AND ANTIMONY IN SILICATE MATERIALS

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The polarographic behavior of arsenic and antimony has been the subject of many papers [1-5]; it has been suggested that these elements can be determined polarographically in production solutions in alcoholic-sulfuric acid media [6]. The arsenic and antimony concentrations examined, however, are usually greater than 0.1 mg/ml.

In the work described here a study was made of the conditions for the polarographic determination of microgram amounts of arsenic and antimony, and a technique has been developed for the preliminary concentration of these elements. The method can be used for the determination of arsenic and antimony in quartz and in silicates rich in silicon.

TABLE 1

Results of Determinations of the Loss of Arsenic and Antimony (The amount of SiO_2 was 1 g in all the experiments)

As added, μg	As found, μg	Error, %	Sb added, μg	Sb found, μg	Error, %
1	0.97	—3	1	0.98	—2
5	5.4	8	2	1.78	—10
10	9.3	—7	10	9.8	—2
25	24.5	—2	25	24.2	—3
50	48.0	—4	50	47.3	—5

The elements are separated by distilling them as their chlorides after decomposing aliquots with a mixture of hydrofluoric and sulfuric acids; this technique has been used before [7] for the separation of arsenic and antimony. Since, in the given instance, arsenic and antimony are to be determined in the same solution, their separation during distillation is unnecessary, and this appreciably simplifies the process.

Control of losses which occur during isolation was effected by means of radioactive indicators. For contents of the test elements $\geq 10^{-4}\%$, the loss does not amount to more than 10% (Table 1).

All the materials used were carefully purified, the degree of purification being checked polarographically (the amount of impurities left after purification whould lie outside the sensitivity limits of the polarographic method). Distilled water passed through a column of the cation exchange resin KU-2 was

* See English translation.